

Using $^{31}\text{P}\{^1\text{H}\}$ Cross Polarization MAS NMR to Probe the Surface Dissolution of Phosphate Glasses

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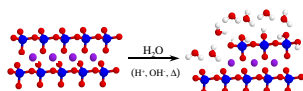
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Background

The dissolution process in alkali phosphate glasses has been probed using $^{31}\text{P}\{^1\text{H}\}$ Cross Polarization (CP) MAS NMR techniques. By utilizing the magnetization of protons that originate directly from the hydration layer involved in the dissolution of the glass, it is possible to filter or select ^{31}P signals that originate from the aged surface. This filtering allows the chemistry of the aged surface to be probed independently from the unaged bulk glass material.

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Dissolution in Phosphate Glasses

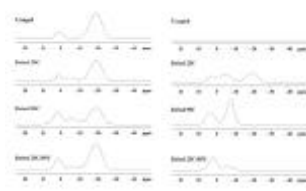


- Can the structural changes due to dissolution be determined?
- Can the reactive species be distinguished and identified?

^1H - ^{31}P CPMAS NMR provides a tool to investigate these surfaces.

Direct

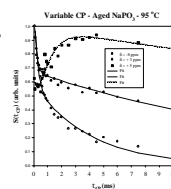
^1H - ^{31}P CP



• Analysis of the multi-component cross-polarization dynamics allows different hydrogen binding motifs to be separated.

• The resonances at $\delta = -8$ and $+3$ ppm show very quick CP transfer supporting the assignment of strong hydrogen bonds for these Q^1_{int} and Q^1_{int} resonances. For the Q^1_{int} this suggests intramolecular hydrogen bonding to Q^1_{int} groups.

• The resonance at $\delta = +5$ ppm shows a slower CP transfer suggesting that this Q^1 species has a weaker intermolecular hydrogen bond.



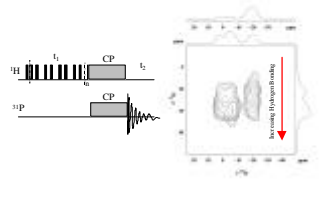
^1H - ^{31}P Heteronuclear Correlations Experiments

Correlation of the ^{31}P and ^1H chemical shift allows the separation and identification of 7-8 different phosphate species in aged glass. Increases in ^1H chemical shift are generally associated with increases in the strength of the hydrogen bonding involved.

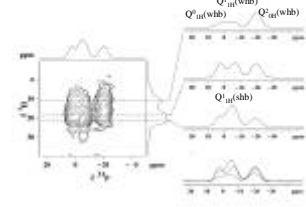
The quantity and type of species present strongly depends on the drying conditions following the initial aging under water. For example compare the sample dried under ambient conditions versus those dried at 95°C .

Under ambient drying, both intra- and inter-hydrogen bonding motifs are observed, including correlation to Q^2 species ($\delta = -20$ ppm). This species contains no OH as a result of depolymerization compared to the Q^1_{int} species ($\delta = -8$ ppm). At least 2 different Q^1_{int} and 2 different Q^1_{ext} species are observed.

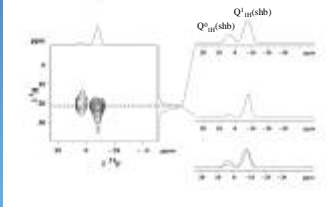
^1H - ^{31}P Heteronuclear Correlation



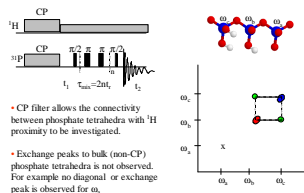
Aged Metaphosphate Glass - Ambient



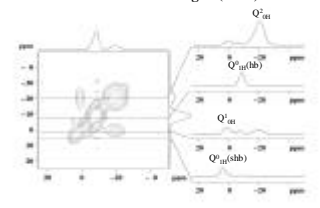
Aged Metaphosphate Glass - 95°C



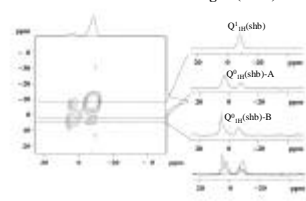
$^1\text{H}\{^{31}\text{P}\}$ CP-Filtered 2D ^{31}P - ^{31}P RFDR Experiment



2D RFDR - Direct on Aged (95°C)



2D RFDR - CP Filtered on Aged (95°C)



Summary

$^{31}\text{P}\{^1\text{H}\}$ provides detailed information about the chemical species present during dissolution of phosphate glasses

^1H - ^{31}P heteronuclear correlation experiments allow 7-8 different phosphate species to be identified within the aged glass.

Using the ^1H - ^{31}P as a pre-filter to dipolar exchange type experiments, allowing the connectivity between these different species is more easily evaluated.